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Self-organized ZnO quantum dots on SiO₂/Si substrates by metalorganic chemical vapor deposition

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ZnO quantum dots (QDs) were fabricated on SiO₂/Si substrates by metalorganic chemical vapor deposition. The densities and sizes of dots were investigated by atomic force microscopy. Photoluminescence at 10 K showed the broad spectra with band tails up to about 3.55 and 3.65 eV for the as-grown and the annealed ZnO QDs, respectively, which were located at the higher energy with respect to the free exciton emission of the ZnO thin film located at about 3.377 eV. These results indicate that the broad emission band results from the quantum size effect, reflecting the dot size inhomogeneity. © 2002 American Institute of Physics. [DOI: 10.1063/1.1527690]

ZnO has attracted attention as a promising material with a wide band gap of 3.37 eV at room temperature for short-wavelength optical device applications.^{1,2} Due to the remarkable excitonic properties of ZnO, such as large exciton binding energy (60 meV) and biexciton binding energy (15 meV),^{3–5} many significant exciton effects may be expected in low-dimensional ZnO nanostructures. Therefore, the realization of ZnO nanostructure with quantum size effects is strongly demanded. There have been reports focused on the ZnO nanostructure such as nanowires,^{6,7} nanorods,^{8,9} and nanoparticles.^{10–12} However, except for nanoparticles fabricated by either electrochemical deposition methods^{10,13} or powder chemical reactions,^{11,12} there have been few reports to confirm quantum size effects in ZnO nanostructures grown by using a conventional semiconductor growth method, such as molecular beam epitaxy or metalorganic chemical vapor deposition (MOCVD). In this regard, a promising technology to achieve efficient quantum confine characteristics in ZnO-based II-oxide semiconductors would be highly desirable.

In previous work,¹⁴ we have shown that the self-organized growth of nanometer-sized ZnO islands on SiO₂/Si substrates could be accomplished by the vertical geometry MOCVD system by means of nitrous oxide (N₂O) as an oxygen precursor and diethylzinc (DEZn) as a zinc source by varying growth conditions. However, we could not observe the quantum size effect in the ZnO nanoislands. This was because the islands were too big (width > 40 nm and height > 10 nm) to cause the quantum size effect. In this letter, using a different oxygen source, nitrogen dioxide (NO₂), we report on the fabrication and characterization of self-organized ZnO quantum dots (QDs) with smaller sizes and higher densities capable of resulting in apparent quantum size effects grown on SiO₂/Si substrates by MOCVD.

The self-organized ZnO QDs in this work were grown on thermally formed SiO₂ layers with a thickness of 25 nm on Si (111) substrates by MOCVD, where DEZn as a zinc source and reactive NO₂ gas as an oxygen source were used. The flow rates of DEZn and NO₂ were optimized at 3 and 100 μmol/min, respectively. The total pressure was fixed at 10 Torr. The surface morphologies of the ZnO dots were investigated by atomic force microscopy (AFM) in a contact mode. Photoluminescence (PL) was measured using 325 nm

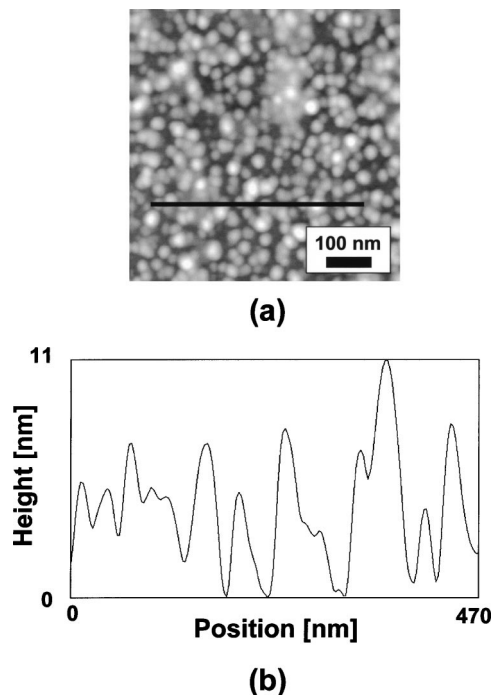


FIG. 1. 600×600 nm² AFM image of ZnO QDs grown on the SiO₂/Si (111) substrate at 550 °C for 90 s. (a) plan-view image of QDs (b) the linearly scanned profile of the surface morphology along the solid line marked in the Fig. 1(a).

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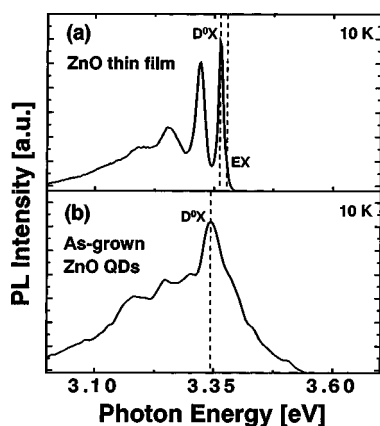


FIG. 2. PL spectra of the ZnO thin film and QDs grown on the SiO₂/Si (111) substrate at 550 °C measured at 10 K. (a) ZnO thin film grown for 60 min and (b) ZnO QDs grown for 90 s.

line of a He–Cd laser (10 mW) as an excitation source, which was dispersed with a 1 m double monochromator and processed utilizing time-correlated single-photon-counting electronics.

Figure 1 shows an AFM image of ZnO QDs grown at 550 °C for 90 s. Here, the dot density is $1.8 \times 10^{11} \text{ cm}^{-2}$, the average height is 6 nm, and the average width is 31 nm. PL spectra recorded at 10 K from the ZnO thin film and ZnO QDs on the SiO₂/Si substrates grown at 550 °C for 60 min and 90 s, respectively, are presented in Fig. 2. In the PL spectrum from the ZnO thin film, a shoulder peak at 3.377 eV labeled “EX” and a sharp peak labeled “D⁰X” are attributed to the free exciton emission and the neutral donor-bound exciton emission, respectively. However, regarding three peaks located at lower energy position of D⁰X, we cannot precisely explain the origin of the luminescence at present. Since they are omnipresent in our ZnO samples grown on Si substrates and SiO₂/Si substrates, we speculate that the emissions are associated with structurally induced defects. For the ZnO QDs, we observed the broad emission band with a tail up to about 3.55 eV located at a higher energy with respect to band edge emission of ZnO thin films, where the free exciton emission is generally located at about 3.377 eV. This is an indication that the experimentally observed band-gap enhancement results from low-dimensional quantum confinement effects. However, the D⁰X emission from the ZnO QD sample, which is probably from large dots, is somewhat redshifted which might be due to the insufficient crystal and optical properties of ZnO dots.¹⁴

The band gap enhancement according to effective mass theory assuming infinite potential barriers to clarify quantum size effects was theoretically investigated. The band gap enhancement ΔE for low-dimensionally confined ZnO QDs is approximately given by

$$\Delta E \approx \frac{\pi^2 \hbar^2}{2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \left(\frac{1}{l^2} + \frac{2}{w^2} \right),$$

where l and w is the dot height and width, respectively. The effective masses of electrons and holes are $m_e^* = 0.24m_0$ and $m_h^* = 0.45m_0$ respectively for ZnO.¹⁰ Thus, the energy E of the free exciton emission from ZnO QDs may be given by

$$E \approx E_{\text{EX,ZnO}} + C \left(\frac{1}{l^2} + \frac{2}{w^2} \right),$$

neglecting the enhancement of exciton binding energy in QDs. Here, $E_{\text{EX,ZnO}}$ is 3.377 eV as shown in Fig. 2(a), and C is the calculated confinement parameter as 2.40 if l and w are expressed in nanometers. Substituting the average height of 6 nm and the average width of 31 nm, which were revealed from Fig. 1, the calculated emission energy is 3.45 eV, which somewhat agrees with the experimental PL result shown in Fig. 2(b). However, in spite of the size inhomogeneity and the large density in the order of 10^{11} cm^{-2} of QDs, the emission band from quantum size effects in ZnO QDs is not broad, but rather has just appeared as the band tail.

In general, the luminescence of a QD originates from carriers generated in the surrounding barrier diffusing into the QD, and from the carriers generated in the QD. However, with almost no expected diffusion of carriers from SiO₂ to the ZnO QDs, the luminescence from the QDs is attributed mainly to carriers generated within the QDs, leading to quantum size effects. Therefore, the structural and optical qualities of ZnO QDs are greatly important in order to achieve efficient quantum size effects in our system, which indicates that ZnO nanoislands with amorphous and/or polycrystalline structure can act as nonradiative recombination centers and can diminish the efficiency of the emissions with quantum size effects from ZnO QDs.

ZnO has a strong ionic bonding nature, similar to that of ionic compounds. Thus, the high binding energy between ZnO and SiO₂ and use of reactive NO₂ as an oxygen source in ZnO growth can easily make ZnO deposition in the initial stage of growth. However, we suggest that initial ZnO on amorphous SiO₂ is not epitaxy, which means that the a -axis of the initial ZnO islands is randomly rotated in the plane of the substrate. Actually, amorphous ZnO island structures have been observed in the literature.^{15–17} The ZnO QDs with a c -axis preferred orientation are then formed by releasing the initially accumulated strain energy in order to achieve crystallinities of themselves. However, the absence or presence of a ZnO wetting layer could not be confirmed by AFM. More detailed studies, such as surface analysis using transmission electron microscopy, will be reported to precisely explain the mechanism of the formation of these ZnO QDs.

Considering the fact that we carried out post-growth annealing of these ZnO QDs aiming at improving the crystallinity. The thermal annealing was carried out at 800 °C for 3 min in an oxygen atmosphere in a furnace. Figure 3(a) shows the AFM image of thermally annealed ZnO QDs with the dot density of $8 \times 10^{10} \text{ cm}^{-2}$, the average height of about 8 nm, and the average width of about 34 nm. The dot density slightly decreased and the dot size increased by the thermal treatment, which can be easily explained by the coalescence of dots. In order to calculate the exact band gap enhancement by quantum size effects, the heights and widths of all the dots were investigated by AFM and were plotted in Fig. 3(b). The average ratio of height and width is about 0.25 obtained by the linear fitting of all the points, demonstrating the lens-like shape of these ZnO QDs.

The PL spectrum measured at 10 K from annealed ZnO QDs is presented at Fig. 4. The emission band over the band AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

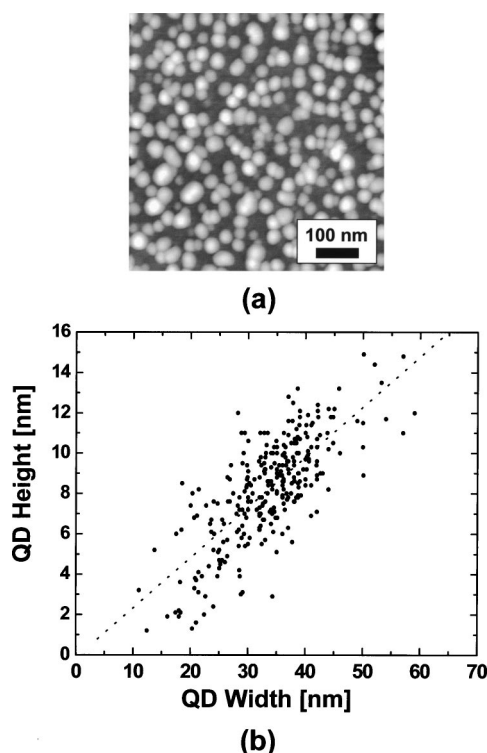


FIG. 3. $600 \times 600 \text{ nm}^2$ AFM image and size distribution of ZnO QDs which were grown at 550°C for 90 s followed by annealing at 800°C for 3 min in an oxygen atmosphere. (a) plan-view image of QDs and (b) dot size distribution of individual QDs. The dotted line in the Fig. 3(b) is the slope obtained by the linear fitting of all the points, demonstrating the approximate ratio of height and width of individual dots.

gap of the ZnO thin film [Fig. 2(a)] was quite enlarged toward a much higher energy region (3.65 eV) compared to that from as-grown ZnO QDs. To confirm whether the emission band is originated by quantum size effects from ZnO QDs, we calculated the transition energies of each annealed ZnO QD by inserting all the values of widths and heights plotted in Fig. 3(b) into the previous equation. The number

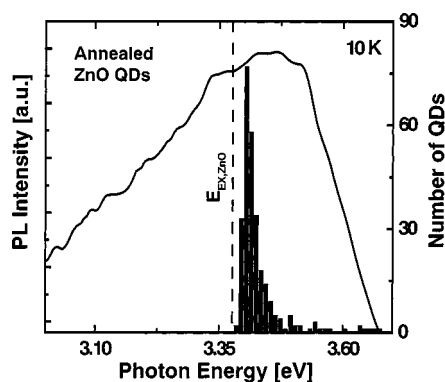


FIG. 4. PL spectrum measured at 10 K and histogram of the expected emission energy in terms of the dot size distribution. The AFM image of this sample is presented at Fig. 3(a) and the histogram of the dot size distribution was drawn using the result of Fig. 3(b). The dashed line indicates the free exciton energy position (3.377 eV) of the ZnO thin film.

of dots having the certain transition energy is then plotted as a histogram as shown with the vertical bars in Fig. 4. Based on this estimation method, the transition energies from the calculated result that depends on the AFM image, are lower than the PL spectrum measured at 10 K (See Fig. 4), which might be due to overestimation of dot sizes caused by an AFM tip.¹⁸ Moreover, considering smaller sizes of as-grown ZnO QDs than those of annealed ZnO QDs, the PL results are controversial. The problem might be explained by the improvement of crystal and optical properties of small ZnO QDs with quantum confinement characteristics due to the annealing treatment. On the other hand, the emission band below the band gap of bulk ZnO becomes broad, which might be attributed to defects in QDs.

In summary, we have achieved the formation of ZnO QDs with quantum size effects on SiO_2/Si substrates by MOCVD. It has been confirmed by AFM studies that the size and density of ZnO QDs can be controlled by growth conditions. We have ascertained quantum size effects in ZnO QDs by PL analysis. The post-growth annealing treatment showed an improvement of structural and optical properties and lead to achieving efficient quantum confinement characteristics from the ZnO QDs.

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